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July 11, 2005

International Conference on Computational Methods in
Science and Engineering
Loutraki, Korinthos, Greece
October 21, 2005 through October 26, 2005

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Water Under the Extreme Conditions of Planetary Interiors: Symmetric Hydrogen Bonding in the Superionic Phase

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Received 8 July, 2005; accepted in revised form XX July, 2005

Abstract: The predicted superionic phase of water is investigated via *ab initio* molecular dynamics at densities of 2.0-3.0 g/cc (34 -115 GPa) along the 2000K isotherm. We find that extremely rapid (superionic) diffusion of protons occurs in a fluid phase at pressures between 34 and 58 GPa. A transition to a stable body-centered cubic (bcc) O lattice with superionic proton conductivity is observed between 70 and 75 GPa, a much higher pressure than suggested in prior work. We find that all molecular species at pressures greater than 75 GPa are too short lived to be classified as bound states. Above 95 GPa, a transient network phase is found characterized by symmetric O-H hydrogen bonding with nearly 50% covalent character.

Keywords: superionic, water, ab initio, molecular dynamics, planetary interiors

Mathematics Subject Classification: 70F20, 74N25, 82B10, 85A99

PACS: 61.20Ja, 31.15Ar, 71.15Pd, 62.50+p

The density profiles of large planets, such as Uranus and Neptune, suggest that there exists within a thick layer of “hot ice”, which is thought to be 56% H₂O, 36% CH₄, and 8% NH₃[1]. This has lead to a theoretical prediction of a superionic phase of water[2, 3], wherein the oxygen atoms have formed a bcc lattice, and the hydrogens diffuse at rates comparable that of the ambient liquid. However, these results have been controversial, both in terms of theory[4] and experiment[5, 6, 7]. Here, we investigate the superionic phase of water with extensive first principles Car-Parrinello molecular dynamics simulations, the results of which have been published previously[8]. Calculated power spectra (i. e., the vibrational density of states, or VDOS) have recently been compared to measured experimental Raman spectra[9] at pressures up to 55 GPa and temperatures of 1500K. The agreement between theory and experiment was very good. In particular, weakening and broadening of the OH stretch mode at 55 GPa was found both theoretically and experimentally.

For our simulations, we used the CPMD code v.3.91, the details of which have already been published[8]. Initial conditions were generated in two ways: 1) a liquid configuration at 2000K was compressed from 1.0 g/cc to the desired density in sequential steps of 0.2 g/cc from an equilibrated sample. 2) An ice VII configuration was relaxed at the density of interest, then heated to 2000K in steps of 300 degrees each for a duration of 0.5 – 1 ps. While heating the temperature was controlled via velocity scaling. We will refer to the first set of simulations as the “L” set, and the second

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as the “S” set. Unless stated otherwise, the results (including the pressures) from the “S” initial configurations are those reported. Once the desired density and/or temperature were achieved, all simulations were equilibrated for a minimum of 2 ps. Data collection simulations were run from 5–10 ps, the results of which are discussed below.

The calculated diffusion constants for both “L” and “S” simulations are virtually identical up until 2.6 g/cc. At 34 GPa (2.0 g/cc), the hydrogen atom diffusion constant has achieved values associated with superionic conductivity (greater than 10^{-4} cm²/s). The diffusion constant remains relatively constant with increasing density, in qualitative agreement with the experimental results of Chau et al.[6] for the ionic conductivity. On the other hand, the O diffusion constant drops to zero at 75 GPa (2.6 g/cc) for both “L” and “S” initial configurations. The surprisingly small hysteresis in the fluid to superionic transition allows us to place the transition point between 70 GPa (2.5 g/cc) and 75 GPa (2.6 g/cc).

Analysis of the oxygen-oxygen RDF for the “S” simulations for all pressures yields a coordination number of the first peak of just over 14, consistent with a high density bcc lattice in which the first two peaks are broadened due to thermal fluctuations. The RDF was further analyzed by calculating an “average position” RDF in which the position of each oxygen was averaged over the course of the trajectory. The results for 75 – 115 GPa indicate the presence of bcc lattice undergoing large amplitude vibrations, even though the RDF’s have width similar to that of a liquid or a glass. The RDFs for the amorphous phase are similar to those of the solid phase obtained in the “S” simulations.

We have determined the free energy barrier for dissociation by defining a free energy surface for the oxygen-hydrogen distances, viz. $W(r) = -k_B T \ln[g(R_{OH})]$, where $W(r)$ is the free energy surface (potential of mean force). We have analyzed the chemical species prevalent in water at these conditions. We define instantaneous species based on the O–H bond distance. If the bond distance is less than a value r_c , we count the atom pair as bonded. Determining all the bonds in the system gives the chemical species at each point in time. Species with lifetimes less than an O–H bond vibrational period (10 fs) are “transient”, and do not represent bound molecules. The optimal cutoff r_c between bonded and non-bonded species is given by the location of the maximum in the free energy surface[10].

The use of the free energy maximum to define a bond cutoff provides a clear picture of qualitative trends. As expected from the $g(R_{OH})$, at 34 GPa, the free energy peak is found at 1.30 Å, which is approximately the same value obtained from simulations of ambient water. At 75 GPa, the free energy peak maintains almost the same position, but broadens considerably. At 115 GPa, the peak has sharpened once again, and the maximum is at 1.70 Å.

Given the above definition of a bond distance, we have analyzed species lifetimes. Above 2.6 g/cc, the lifetime of all species is less than 12 fs, which is roughly the period of an O–H bond vibration (ca. 10 fs). Hence, water above 75 GPa and at 2000K does not contain any molecular states, but instead forms a collection of short-lived “transient” states. The “L” simulations at 2.6 g/cc (77 GPa) and 2000K yield lifetimes nearly identical to that found in the “S” simulations described above (within 0.5 fs). This indicates that the amorphous states formed from the “L” simulations are closely related to the superionic bcc crystal states found in the “S” simulations.

Species concentrations were calculated for all simulations. At 34 GPa (2.0 g/cc), H₂O is the predominant species, with H₃O⁺ and OH[−] having mole fractions of ca. 5%. In addition, some aggregation has occurred in which neutral and ionic clusters containing up to six oxygens have formed. The concentrations of OH[−] and H₃O⁺ is low for all densities investigated, and non-existent at 95 and 115 GPa (2.8 and 3.0 g/cc). The calculated lifetimes for these species is well below 10 fs for the same thermodynamic conditions (less than 8 fs at 34 GPa). At pressures of 95 and 115 GPa, the increase in the O–H bond distance leads to the formation of extensive bond networks (Figure 1). These networks consist entirely of O–H bonds, while O–O and H–H bonds were not found to be present at any point.

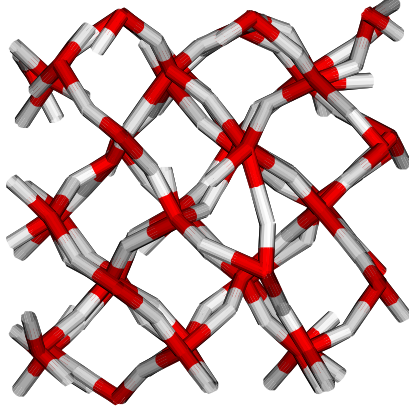


Figure 1: Snapshot of the simulations at 115 GPa. A well defined network has been formed, and the protons dissociate very rapidly, continually breaking and reforming bonds.

Maximally localized Wannier centers[11] of several trajectories were calculated, and a distribution function was determined. The outer peak at 0.46–0.50 Å corresponds to electrons participating in a covalent bond. Based on the above distribution, one can define the minimum at roughly 0.42 Å as a dividing surface wherein a maximally localized Wannier center located at distances shorter than this, relative to its parent oxygen atom, represents a lone pair, and those found at greater distances represent covalent bonds[4]. We used this definition to compute the percentage of O–H bonds with a Wannier center along the bond axis. Surprisingly, the results for pressures of 34 – 75 GPa consistently showed that 85-95% of the O–H bonds are covalent. For 95 and 115 GPa, we find about 50 – 55% of the bonds are covalent. This is consistent with symmetric hydrogen bonding, for which the split between ionic and covalent bonds would be 50/50.

In conclusion, we have performed first principles simulations of water at pressures up to 115 GPa (3.0 g/cc) and 2000K. Along this isotherm we can define three different phases. First, from 34 GPa to 58 GPa (2.0-2.4 g/cc), we observe a molecular fluid phase with superionic diffusion of the hydrogens. Second, at 75 GPa (2.6 g/cc), we find a stable bcc oxygen lattice with superionic proton conduction. O–H bonds within this “solid” phase are found to be mostly covalent, despite their exceedingly short lifetimes of ca. 10 fs. Third, at 95 – 115 GPa (2.8 – 3.0 g/cc) we find a transformation to a phase dominated by transient networks of symmetric O–H hydrogen bonds. Given the smooth nature of the calculated P–V isotherm, the transition to the network phase does not appear to be first order. The network can be attributed to the symmetrization of the hydrogen bond, similar to the ice VII to ice X transition

Acknowledgment

The authors wish to thank the anonymous referees for their careful reading of the manuscript and their fruitful comments and suggestions. This work was performed under the auspices of the U. S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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